

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 January 2002 (24.01.2002)

PCT

(10) International Publication Number
WO 02/06428 A1

(51) International Patent Classification⁷: C10L 1/14, 10/00

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(21) International Application Number: PCT/US01/22520

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(22) International Filing Date: 18 July 2001 (18.07.2001)

(81) Designated State (national): US.

(25) Filing Language: English

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(26) Publication Language: English

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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A1

(54) Title: ADDITIVE COMPOSITION FOR MIDDLE DISTILLATE FUELS AND MIDDLE DISTILLATE FUEL COMPOSITIONS CONTAINING SAME

WO 02/06428

(57) Abstract: Additive compositions for improving middle distillate fuel oils comprise (A) from about 35 to about 55 parts by weight of a hydrocarbyl substituted monosuccinimide dispersant containing from about 30 to about 200 carbon atoms in the hydrocarbyl group and (B) from about 75 to about 40 parts by weight of an oil having viscosity ranging from about 100 to about 400 centistokes at 40 °C, fuel compositions comprising a major amount of a middle distillate fuel oil and a sufficient amount of the additive composition to provide from about 35 to about 55 parts by weight of (A) a hydrocarbyl substituted monosuccinimide dispersant containing from about 30 to about 200 carbon atoms in the hydrocarbyl group and from about 75 to about 40 parts by weight of (B) an oil having viscosity ranging from about 100 to about 400 centistokes at 40 °C, per million parts by weight of fuel oil, a method for reducing fouling of fuel oil injectors comprising fueling a device equipped with said injectors with the fuel composition of the invention, and a method of operating a compression-ignition engine comprising providing as the fuel the fuel oil composition of this invention thereby reducing fouling of fuel oil injectors of said engine.

5 TITLE: ADDITIVE COMPOSITION FOR MIDDLE DISTILLATE FUELS AND
MIDDLE DISTILLATE FUEL COMPOSITIONS CONTAINING SAME

FIELD OF THE INVENTION

This invention relates to additive compositions for middle distillate fuels and middle distillate fuel compositions which exhibit markedly reduced fuel injector deposit forming tendencies.

10 BACKGROUND OF THE INVENTION

Middle distillate fuels are used in a number of applications such as in heating equipment and in engines, for example jet engines and diesel engines. The fuels are frequently supplied to the combustion chamber via fuel injectors. Since the injectors are in close proximity to the combustion chamber, they are exposed to high 15 temperatures. Deposits can form arising from degradation of the fuel being exposed to elevated temperatures.

20 Fuel additives are employed to improve performance. A wide variety of additives are known, including cetane number improvers which improve the ignition quality of the fuel, stabilizers, smoke reducing additives, corrosion inhibitors and detergents/dispersants.

25 Diesel engines are compression ignition engines. Compression of the air/fuel mixture within the combustion chamber generates the heat required to ignite the fuel. In the diesel combustion process, fuel vaporization and efficient mixing with available air are essential in insuring efficient combustion. The fuel injection equipment provides the mechanical means of achieving this and its performance is critical in controlling rate of fuel injection and atomization. Optimum performance is only achieved when the fuel injection system is free from deposits and is adjusted in accordance with the manufacturer's specifications. As noted, there is a tendency 30 for fuels to form deposits during distribution and combustion. These deposits can markedly affect the combustion process.

Critical deposits can form in two basic areas. A buildup of gum or resinous degradation products can occur in the injection system. Problems often occur on

isolated cylinders of an engine, the resultant misfiring causing loss of power and increased exhaust smoke. Carbon deposits on parts of injectors exposed to hot combustion gases affect both fuel flow and atomization. Loss of power, increased exhaust smoke and poor starting are noticeable engine performance problems.

5 Deposits can form in other areas exposed to the fuel.

Fouling of diesel fuel injector nozzles by fuel and oil decomposition products leads to imperfect fuelling in terms of amount and spray direction of fuel delivered to the combustion chamber. Driveability difficulties, reduced fuel economy, adverse emissions performance and cylinder liner wear are some of the 10 possible consequences of such fouling.

Chemical additives have been used to control formation of deposits. Commonly, these are dispersants of the ashless type, that is, they are essentially free of metal. Generally, the additives have been various nitrogen-containing compounds.

15 Cost is a major consideration when materials are being considered as performance improving additives for fuels. Dispersants are generally used at minimal levels to provide acceptable performance. Oil and other diluents are frequently used in minimum amounts, as diluents for dispersants to facilitate handling thereof, e.g., reduce viscosity, etc. These diluents are typically light oil 20 fractions, for example 100 solvent neutral oils. The oils used as diluents normally are not considered as having any significant effect on detergency or dispersancy.

Sugimoto, U.S. Patent 6,051,039 describes diesel fuel compositions containing an additive composition made by mixing or reacting A) at least one dicarboxylic acid having about 8-500 carbon atoms or a reactive equivalent thereof 25 and B) at least one amine having about 6 to about 80 carbon atoms and optionally, at least one monocarboxylic acid of about 8 to about 28 carbon atoms or a reactive equivalent thereof.

Dorer, U.S. Patent 3,658,494 teaches fuel compositions comprising a major amount of a normally liquid fuel and a minor amount of an additive combination 30 comprising at least one oxy compound selected from monoethers of glycols and polyglycols and at least one fuel-soluble dispersant, including, inter alia imides of

substantially saturated carboxylic acids characterized by the presence within the acyl radical of at least 30 aliphatic carbon atoms.

We have now found that mixtures of monosuccinimide type dispersants and oils within a certain viscosity range used in particular relative amounts provide 5 surprisingly improved cleanliness of injectors in diesel engines and other middle distillate fueled devices.

SUMMARY OF THE INVENTION

This invention is directed to an additive composition for improving middle distillate fuel oils comprising (A) from about 35 to about 55 parts by weight of a 10 hydrocarbyl substituted monosuccinimide dispersant containing from about 30 to about 200 carbon atoms in the hydrocarbyl group and (B) from about 75 to about 40 parts by weight of an oil having viscosity ranging from about 100 to about 400 centistokes at 40°C. In one embodiment, the invention is directed to a fuel composition comprising a major amount of a middle distillate fuel oil and a 15 sufficient amount of the additive composition to provide from about 35 to about 55 parts by weight of (A) a hydrocarbyl substituted monosuccinimide dispersant containing from about 30 to about 200 carbon atoms in the hydrocarbyl group and from about 75 to about 40 parts by weight of (B) an oil having viscosity ranging from about 100 to about 400 centistokes at 40°C, each per million parts by weight of 20 fuel oil. In another embodiment the invention is directed to a method for reducing fouling of fuel oil injectors comprising fueling a device equipped with said injectors with the fuel composition of the invention. In another embodiment, the invention is directed to a method of operating a compression-ignition engine comprising providing as the fuel the fuel oil composition of this invention thereby reducing 25 fouling of fuel oil injectors of said engine.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As used herein, the term "hydrocarbon" means a group which is purely hydrocarbon, that is, a compound of hydrogen and carbon containing no hetero atoms. The terms "hydrocarbyl" or "hydrocarbon based" mean that the group being 30 described has predominantly hydrocarbon character within the context of this invention. Hydrocarbyl groups and hydrocarbon based groups include groups that are purely hydrocarbon in nature, that is, they contain only carbon and hydrogen.

They may also include groups containing non-hydrocarbon substituents or atoms which do not alter the predominantly hydrocarbon character of the group. Such substituents may include halo-, alkoxy-, nitro-, etc. These groups also may contain hetero atoms. Suitable hetero atoms will be apparent to those skilled in the art and 5 include, for example, sulfur, nitrogen and oxygen. Therefore, while remaining predominantly hydrocarbon in character within the context of this invention, these groups may contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms. Thus, the terms "hydrocarbyl" and "hydrocarbon based" are broader than the term "hydrocarbon" since all hydrocarbon groups are 10 also hydrocarbyl or hydrocarbon based groups while the hydrocarbyl or hydrocarbon based groups containing hetero atoms are not hydrocarbon groups.

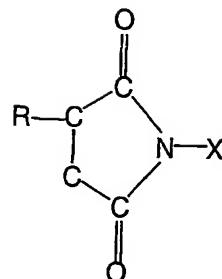
In general, no more than about three non-hydrocarbon substituents or hetero atoms, and preferably no more than one, will be present for every 10 carbon atoms in the hydrocarbyl or hydrocarbon based groups. Most preferably, the groups are 15 purely hydrocarbon in nature, that is they are essentially free of atoms other than carbon and hydrogen.

The hydrocarbyl and hydrocarbon based groups are preferably free from acetylenic unsaturation; ethylenic unsaturation, when present will generally be such that there is no more than one ethylenic linkage present for every ten carbon-to-carbon 20 bonds. The groups are often completely saturated and therefore contain no ethylenic unsaturation.

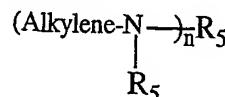
As used in the specification and in the appended claims, the singular forms "a", "an" and "the" include plural unless the context clearly dictates otherwise. Thus, for example, reference to a polymer includes mixtures of polymers, reference to an 25 acylating agent includes mixtures of acylating agents, etc.

Hydrocarbyl Substituted Succinimide Dispersant

As noted herein the compositions of this invention comprise a hydrocarbyl substituted monosuccinimide dispersant containing from about 30 to about 200 carbon atoms in the hydrocarbyl group. These can be represented by the general 30 formula



wherein R is the hydrocarbyl substituent and X is selected from the group consisting of H, hydrocarbyl containing from 1 to about 30 carbon atoms, preferably aliphatic hydrocarbyl, -alkylene-OR³ wherein R³ is H or hydrocarbyl, preferably H or lower alkyl, and groups of the formula



wherein n has an average value between about 1 and about 10, the "Alkylene" group has from 1 to about 10 carbon atoms, and each R₅ is independently hydrogen or an aliphatic group or a hydroxy substituted or an amino aliphatic group containing up to 10 about 30 carbon atoms. Preferably the "Alkylene" group is an ethylene or propylene group.

Monosuccinimides used in this invention are prepared by methods well known in the art. They are typically prepared by reacting a hydrocarbyl group substituted succinic acylating agent with ammonia or at least one amine having at least one 15 condensable H-N< group.

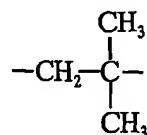
Hydrocarbyl group substituted succinic acylating agents used in the preparation of the monosuccinimide dispersants used in this invention are hydrocarbyl group substituted succinic acids and reactive equivalents thereof. A reactive equivalent is a reactant that will react in a fashion similar to a hydrocarbyl group substituted succinic acid to form derivatives that are essentially the same as those obtained from the succinic acid. For example, anhydrides, lower alkyl esters, acid-lower alkyl ester and acyl halides will react with amines to form substantially similar products as the corresponding acids. Anhydrides, lower alkyl esters, acid-lower alkyl esters and acyl halides are all considered to be reactive equivalents to the 20 corresponding succinic acid.

The group 'R' is a hydrocarbyl group, preferably a hydrocarbon based group. More preferably, the group 'R' is an aliphatic group. The hydrocarbyl group 'R' contains from about 30 to about 200 carbon atoms, often from about 30, more often from about 50 up to about 100 carbon atoms. The hydrocarbyl group is most 5 preferably an aliphatic group derived from homopolymerized and interpolymerized polyolefins, wherein the olefins, usually 1-olefins, contain from about 2 to about 18 carbon atoms. Often the olefins are lower olefins, preferably ethylene, propylene and butenes, typically 1-butene and isobutylene and mixtures thereof, particularly, isobutylene.

10 As used herein, the expression "polyolefin" defines a polymer derived from olefins.

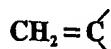
In another preferred embodiment, R is derived from polypropylene. In another preferred embodiment, R is derived from ethylene-alpha olefin polymers, including ethylene- α -olefin-diene polymers, especially those wherein the diene is a 15 non-conjugated diene. Representative of such polymers are the ethylene-propylene copolymers and ethylene-propylene-diene terpolymers.

A preferred source of hydrocarbyl groups R are polybutenes obtained by polymerization of a C₄ refinery stream having a butene content of 35 to 75 weight percent and isobutylene content of 15 to 60 weight percent in the presence of a 20 Lewis acid catalyst such as aluminum trichloride or boron trifluoride. These polybutenes contain predominantly (greater than 80% of total repeating units) isobutylene repeating units of the configuration

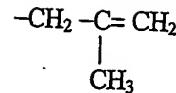


These polybutenes are typically monoolefinic, that is they contain but one olefinic 25 bond per molecule.

In one embodiment, the monoolefinic groups are predominantly vinylidene groups, i.e., groups of the formula



especially those of the formula



although the polybutenes may also comprise other olefinic configurations.

5 In one embodiment the polybutene is substantially monoolefinic, comprising at least about 30 mole %, preferably at least about 50 mole % vinylidene groups, more often at least about 70 mole % vinylidene groups. Such materials and methods for preparing them are described in U.S. Patents 5,071,919; 5,137,978; 5,137,980; 5,286,823 and 5,408,018, and in published European patent application EP 646103-A1, 10 each of which is expressly incorporated herein by reference. They are commercially available, for example under the tradenames ULTRAVIS® (BP Chemicals) and GLISSOPAL® (BASF).

15 In one embodiment, the hydrocarbyl substituent is a polyisobutenyl group having \bar{M}_n ranging from about 400 to about 2,500, more often from about 800 to about 1200.

20 Molecular weights of the polymers are determined using well known methods described in the literature. Examples of procedures for determining the molecular weights are gel permeation chromatography (GPC) (also known as size-exclusion chromatography), light scattering, and vapor phase osmometry (VPO). 25 The GPC technique employs standard materials against which the samples are compared. For best results, standards that are chemically similar to those of the sample are used. For example, for polystyrene polymers, a polystyrene standard, preferably of similar molecular weight, is employed. When standards are dissimilar to the sample, generally relative molecular weights of related polymers can be determined. For example, using a polystyrene standard, relative, but not absolute, molecular weights of a series of polymethacrylates may be determined. These and other procedures are described in numerous publications including:

30 P.J. Flory, "Principles of Polymer Chemistry", Cornell University Press (1953), Chapter VII, pp 266-316, and "Macromolecules, an Introduction to Polymer Science", F.A. Bovey and F.H. Winslow, Editors, Academic Press (1979), pp 296-312.

W.W. Yau, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979.

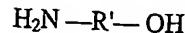
Succinic acylating agents and the production thereof are both well known to those skilled in the art. They are conveniently prepared by reacting a polyolefin with 5 maleic acid or a reactive equivalent thereof. Reactive equivalents are acyl halides, esters, particularly lower alkyl esters, acid-esters, and maleic anhydride. Maleic anhydride is preferred. The reaction can be conducted thermally, i.e., by simply combining and heating the reactants or with the addition of chlorine during the reaction. Alternatively, the maleic reactant can be reacted with a halogenated, 10 usually chlorinated, polyolefin. Monosuccination of the polyolefin is desired. Accordingly, typically from about 0.95 to about 1.1, most preferably 1, moles of maleic acid or reactive equivalent thereof is reacted with one mole, based on \overline{M}_n of polyolefin. Illustrative hydrocarbyl group substituted succinic acylating agents and processes for their production are described in numerous patents including 15 U.S. 3,172,892; U.S. 3,454,607, 3,215,707 and 6,051,039.

Monosuccinimide dispersants are derived by reacting the succinic acylating agents with ammonia or at least one amine having at least one condensable primary amino group.

The amines may be monoamines or polyamines, typically polyamines, 20 preferably ethylene polyamines, amine bottoms or amine condensates. The amines can be aliphatic, cycloaliphatic, aromatic or heterocyclic, including aliphatic-substituted cycloaliphatic, aliphatic-substituted aromatic, aliphatic-substituted heterocyclic, cycloaliphatic-substituted aliphatic, cycloaliphatic-substituted heterocyclic, aromatic-substituted aliphatic, aromatic-substituted cycloaliphatic, 25 aromatic-substituted heterocyclic, heterocyclic-substituted aliphatic, heterocyclic-substituted alicyclic, and heterocyclic-substituted aromatic amines and may be saturated or unsaturated.

Monoamines useful in this invention generally contain from 1 to about 24 carbon atoms, preferably 1 to about 12, and more preferably 1 to about 6. Examples 30 of primary monoamines useful in the present invention include methylamine, propylamine, butylamine, cyclopentylamine, dodecylamine, allylamine, cocoamine and stearylamine.

The monoamine may be an alkanol amine represented by the formula:



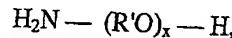
wherein R' is a divalent hydrocarbyl group of about two to about 18 carbon atoms, preferably two to about four carbon atoms. The group -R'-OH in such formulae

5 represents the hydroxyhydrocarbyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group.

Examples of alkanolamines include monoethanolamine, propanolamine, etc.

The hydroxyamines can also be ether N-(hydroxyhydrocarbyl) amines.

10 These are hydroxy poly(hydrocarbyloxy) analogs of the above-described hydroxy amines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyhydrocarbyl) amines can be conveniently prepared, for example, by reaction of epoxides with ammonia and can be represented by the formula:



15 wherein x is a number from about 2 to about 15 and R' is as described above.

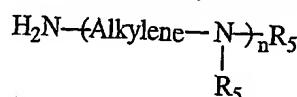
Other useful amines include ether amines of the general formula $\text{R}_6\text{OR}'^1\text{NH}_2$

wherein R_6 is a hydrocarbyl group, preferably an aliphatic group, more preferably an alkyl group, containing from 1 to about 24 carbon atoms, R'^1 is a divalent

20 hydrocarbyl group, preferably an alkylene group, containing from two to about 18 carbon atoms, more preferably two to about 4 carbon atoms. Especially preferred ether amines are those available under the name SURFAM® produced and marketed by Sea Land Chemical Co., Westlake, Ohio.

25 The amine may also be a polyamine. The polyamine may be aliphatic, cycloaliphatic, heterocyclic or aromatic. Examples of useful polyamines include alkylene polyamines, hydroxy containing polyamines, polyoxyalkylene polyamines, arylpolyamines, and heterocyclic polyamines.

Alkylene polyamines are represented by the formula



30 wherein n has an average value between about 1 and about 10, preferably about 2 to about 7, more preferably about 2 to about 5, and the "Alkylene" group has from 1 to

about 10 carbon atoms, preferably about 2 to about 6, more preferably about 2 to about 4. Each R₅ is independently hydrogen, an aliphatic group or a hydroxy-substituted- or amino-substituted- aliphatic group of up to about 30 carbon atoms. Preferably R₅ is H or lower alkyl, most preferably, H.

5 Alkylene polyamines include methylene-, ethylene-, butylene-, propylene-, pentylene- and other polyamines. Higher homologs and related heterocyclic amines such as N-amino alkyl-substituted piperazines are also included. Specific examples of such polyamines are ethylene diamine, diethylene triamine, triethylene tetramine, tris-(2-aminoethyl)amine, propylene diamine, N,N-dimethylaminopropylamine, 10 trimethylene diamine, tripropylene tetramine, tetraethylene pentamine, hexaethylene heptamine, pentaethylenehexamine, aminoethyl piperazine, etc.

15 Higher homologs obtained by condensing two or more of the above-noted alkylene amines are similarly useful as are mixtures of two or more of the aforescribed polyamines provided that the resulting condensed amine contains at least one primary amino group.

17 Ethylene polyamines, such as some of those mentioned above, are preferred. They are described in detail under the heading "Diamines and Higher Amines" in Kirk Othmer's "Encyclopedia of Chemical Technology", 4th Edition, Vol. 8, pages 74-108, John Wiley and Sons, New York (1993) and in Meinhardt, et al, U.S. 20 4,234,435, both of which are hereby incorporated herein by reference for disclosure of useful polyamines. Such polyamines are most conveniently prepared by the reaction of ethylene dichloride with ammonia or by reaction of an ethylene imine with a ring opening reagent such as water, ammonia, etc. These reactions result in the production of a complex mixture of polyalkylene polyamines including cyclic 25 condensation products such as the aforescribed piperazines. Ethylene polyamine mixtures are useful. Heavy polyamines, such as described in U.S. Patent 5,936,041 are also useful.

30 Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave as residue what is often termed "polyamine bottoms". In general, alkylene polyamine bottoms can be characterized as having less than two, usually less than 1% (by weight) material boiling below about 200°C. A typical sample of such ethylene polyamine bottoms obtained from

the Dow Chemical Company of Freeport, Texas, designated "E-100" has a specific gravity at 15.6°C of 1.0168, % nitrogen of 33.15 and a viscosity at 40°C of 121 centistokes. Gas chromatography analysis shows such a sample contains about 0.93% "Light Ends" (most probably diethylenetriamine), 0.72%

5 triethylenetetramine, 21.74% tetraethylenepentamine and 76.61% pentaethylene hexamine and higher (by weight). These alkylene polyamine bottoms include cyclic condensation products such as piperazine and higher analogs of diethylenetriamine, triethylenetetramine and the like.

Another useful polyamine is a condensation product obtained by reaction of 10 at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group. The hydroxy compounds are preferably polyhydric alcohols and amines. Preferably the hydroxy compounds are polyhydric amines. Polyhydric amines include any of the above-described monoamines reacted with an alkylene oxide (e.g., ethylene oxide, propylene oxide, 15 butylene oxide, etc.) having two to about 20 carbon atoms, preferably two to about four. Examples of polyhydric amines include tri-(hydroxymethyl)amine, tri-(hydroxymethyl)amino methane, 2-amino-2-methyl-1,3-propanediol, N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine, and N,N,N',N'-tetrakis(2-hydroxyethyl) ethylenediamine.

20 Polyamine reactants, which react with the polyhydric alcohol or amine to form the condensation products or condensed amines, are described above. Preferred polyamine reactants include triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenhexamine (PEHA), and mixtures of polyamines such as the above-described "amine bottoms".

25 The condensation reaction of the polyamine reactant with the hydroxy compound is conducted at an elevated temperature, usually about 60°C to about 265°C in the presence of an acid catalyst.

30 The amine condensates and methods of making the same are described in Steckel (US Patent 5,053,152) which is incorporated by reference for its disclosure to the condensates and methods of making amine condensates.

The polyamines may be hydroxy-containing polyamines provided that they contain at least one condensable primary amino group. These include hydroxy-

containing polyamine analogs of hydroxy monoamines, particularly alkoxyLATED alkylenepolyamines. Such polyamines can be made by reacting the above-described alkylene amines with one or more of the above-described alkylene oxides.

Specific examples of alkoxyLATED alkylenepolyamines include N-(2-hydroxyethyl) ethylenediamine, N,N-di-(2-hydroxyethyl)-ethylenediamine, mono-(hydroxypropyl)-substituted tetraethylene-pentamine, N-(3-hydroxybutyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the above illustrated hydroxy-containing polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the aforesaid polyamines are also useful.

The polyamines may be polyoxyalkylene polyamines, including polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weights ranging from about 200 to about 2000. Polyoxyalkylene polyamines, including polyoxyethylene-polyoxypropylene polyamines, are commercially available, for example under the tradename JEFFAMINE® from Texaco Chemical Co. U.S. Patent numbers 3,804,763 and 3,948,800 contain disclosures of polyoxyalkylene polyamines and are incorporated herein by reference for their disclosure of such materials.

In another embodiment, the polyamine may be a heterocyclic polyamine. The heterocyclic polyamines include aminoalkyl substituted heterocyclic polyamines such as N-aminoalkyl-thiomorpholines, N-aminoalkylmorpholines, N-aminoalkyl-piperazines, N,N'-bisaminoalkyl piperazines, and mixtures of two or more of these heterocyclic amines. Preferred heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, or nitrogen with oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Aminoalkylsubstituted piperidines, aminoalkylsubstituted piperazines, aminoalkylsubstituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially preferred. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part

of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-amino-ethylpiperazine, and N,N'-diaminoethyl-piperazine.

5 Hydrazine and substituted-hydrazine can also be used to form nitrogen-containing carboxylic dispersants. At least one of the nitrogens in the hydrazine must contain two hydrogens directly bonded thereto. The substituents which may be present on the hydrazine include alkyl, alkenyl, aryl, aralkyl, alkaryl, and the like. Usually, the substituents are alkyl, especially lower alkyl, phenyl, and substituted phenyl such as lower alkoxy-substituted phenyl or lower alkyl-substituted phenyl.

10 Specific examples of substituted hydrazines are methylhydrazine, N,N-dimethylhydrazine, phenylhydrazine, N-(para-nitrophenyl)-hydrazine, N-(para-nitrophenyl)-N-methyl-hydrazine, amino guanidine bicarbonate, and the like.

15 During reaction of the hydrocarbyl substituted succinic acylating agent with the primary amine reactant, non-monosuccinimide may be formed along with monosuccinimide products. These include amine salts, amides, and imidazolines as well as mixtures thereof. Desirably, at least 50 mole % of the succinic acylating agent is converted to monosuccinimide, more preferable at least about 75% is converted to monosuccinimide.

20 To prepare the monosuccinimide from the amines, one or more of the hydrocarbyl substituted succinic acylating agents and one or more amines are heated, optionally in the presence of a normally liquid, substantially inert organic liquid solvent/diluent, at temperatures in the range of from about 50°C up to the decomposition point of any of the reactants or the product, but normally at temperatures in the range of from about 100°C up to about 300°C, provided 300°C

25 does not exceed the decomposition point of a reactant or the product. Temperatures of about 100°C, frequently of about 125°C to about 250°C are normally used. The succinic acylating agent and the amine are reacted in an amount sufficient to provide from about one-half mole up to about 1.1 moles of primary amine per mole of the succinic acylating agent.

30 Succinimide production, including monosuccinimide production, is described in, for example, the following patents: U.S. 2,992,708; U.S. 3,018,291; U.S. 3,024,237; U.S. 3,100,673; U.S. 3,172,892; U.S. 3,219,666 and U.S. 3,272,746.

These patents describe the production of a wide variety of succinimide type dispersants. They are incorporated herein by reference for their disclosure of monosuccinimide dispersants and preparation thereof.

The following examples illustrate several succinimide compounds. The 5 products of Examples 1 and 4 illustrate additive compositions of this invention as well as means for preparing same. It is to be understood that these examples are not intended to limit the scope of the invention. Unless indicated otherwise all parts are parts by weight, temperatures are in degrees Celsius. When amounts are in parts by volume, the relationship between parts by weight and parts by volume is as grams to 10 milliliters. Reactions are conducted under nitrogen. Any filtrations are conducted using a diatomaceous earth filter aid. Analytical values are obtained by actual analysis.

Example 1

15 A succinimide is obtained by reacting polyisobutylene (\overline{M}_n about 1000 having about 90% terminal vinylidene groups (Glissopal 1000, BASF)) succinate with 0.87 moles tetraethylenepentamine (Union Carbide) per succinate group (2.2N per C=O) as a 60% weight active solution in SN350 mineral oil.

Example 2

Part A

20 A 316 stainless steel vessel is charged with 21 parts polyisobutylene having \overline{M}_n about 1,000 and containing about 83-85 mole percent terminal vinylidene groups (Ultravis 10, BP Chemicals), and heated to 170°C. Pressure is set to 200 kilopascal (kPa) and temperature is ramped to 220°C as maleic anhydride introduced. A total of 4 parts (2 moles per mole of polyisobutylene) is added, the first part over 0.25 hour, 25 the remainder over 1.5 hour. The reaction is then heated for 2 hours at 228°C/200 kPa. Full vacuum is then applied and excess maleic anhydride (1.6 part) is removed. The reactor is depressurized with nitrogen and cooled to 150°C and sampled. This sample (0.1 part) is identified as "neat 1000 m.w. PIBSA, unfiltered". The remainder of the material is then transferred to a filter feed vessel and 10 parts 30 hydrocarbon solvent (high boiling 80% aromatic/20% aliphatic solvent, CAROMAX 26 available from Carless Refining and Marketing, U.K.) and 30 parts

filter aid are added. The solution is filtered yielding 33 parts filtrate having saponification number = 99.

Part B

10 parts of the filtrate of Part A of this example is charged to a 316 stainless steel reactor and heated to 175°C. 1.8 parts of HPAX (polyethylene amine still bottoms, Union Carbide, 0.87 moles HPAX, 2.6N per C=O) are added over 4 hours. The exothermic reaction is cooled to 165°C to stop excessive solvent boil over. Distillate collected is 110 parts water and 480 parts solvent, which is replaced with fresh solvent in the product to keep the concentration constant. The reaction is held at 165° for 2 hours yielding 11.7 parts product containing 5.4% N.

Example 3

A 1-liter round-bottomed wide necked flask is charged with 400 parts of the filtrate of Part A of Example 2. The contents of the flask are heated with stirring to 175°C under a positive pressure of nitrogen, at which point tetraethylenepentamine, (52.8 parts, 0.87 moles TEPA per succinic anhydride head group, 2.2N per C=O) are added dropwise via a pressure-equalizing dropping funnel over 0.5 hour. An exotherm of 20°C is observed. The reaction mixture is then maintained at 175°C with stirring and the nitrogen flow increased to aid removal off water for a 3 hours yielding 428.8 parts product containing 4.4%N. The amount of distillate collected is 5 parts water and 9.9 parts solvent.

Example 4

A vessel is charged with 1014.4 parts of the sample labeled "neat 1000 m.w. PIBSA, unfiltered" described in Part A of Example 2) and 434.7 parts of SN350 mineral oil (Total). The materials are mixed by stirring for 0.5 hour at 50°C. The resulting 60% solution is then filtered. A 1-liter round-bottomed flask is charged with 400 parts of the filtrate. The contents of the flask are then heated with stirring to 175°C under a positive pressure of nitrogen, at which point tetraethylenepentamine (TEPA) (51.7 parts, 0.87 moles TEPA per succinic anhydride head group, 2.2N per C=O) are added dropwise via a pressure-equalizing dropping funnel over a period of 0.5 hour. An exotherm of 20°C is observed. The reaction mixture is then maintained at 175°C with stirring and the nitrogen flow increased to

aid removal off water for 3 hours yielding 436.7 parts product containing 3.9% N. The amount of distillate collected is 1.6 parts.

Example 5

5 A succinimide prepared as in Example 1 except amine reactant is used to provide 1.81N per C=O.

Example 6

A succinimide prepared as in Example 1 except the mineral oil is 150N.

The Oil

10 Oils that are useful in this invention may be mineral oils, synthetic oils or vegetable oils. Most often they are mineral oils. The oils have viscosity at 40°C ranging from about 100 centistokes (cSt) frequently from about 200 cSt up to about 400 cSt, more often to about 350 cSt. Especially preferred are oils having viscosity at 40°C ranging from about 300 cSt to about 350 cSt.

15 More thermally stable oils are preferred. Particularly preferred are hydrotreated oils and solvent neutral oils.

The additive compositions of this invention contain from about 75 to about 40 parts by weight of the oil per 35 to about 55 parts by weight of the succinimide dispersant.

Middle Distillate Fuels

20 Middle distillate fuels may be derived from petroleum or from vegetable sources or mixtures thereof. More often, for the purposes of this invention they are petroleum derived materials. Middle distillate fuel oils typically have boiling points ranging from about 80°C to about 500°C. These include heating oils, kerosene, jet fuels and diesel fuels. All of these types of fuels are contemplated as being within 25 the scope of this invention, but diesel fuels are particularly preferred. These are fuel oils boiling in the range from about 160°C up to between about 290°C and about 360°C. Such materials are described in U.S. Patent 5,997,592 issued to Shell Oil Co.

30 Properties of diesel oils and specifications for various grades thereof are given in the publication 'Ready Reference for Lubricant and Fuel Performance', Publication No. 240-94R₅ (August, 1998) The Lubrizol Corporation, pp. 84-92.

Other materials commonly used as performance improving additives for middle distillate fuels, and especially diesel fuels may be incorporated into the compositions of this invention in conventional amounts.. These other materials include cold flow improvers, pour point depressants, storage stabilizers, corrosion inhibitors, cetane improvers, anti-static agents, biocidal additives, smoke suppressants. These additives are well known to those of skill in the art. Examples of several types of these additives are given in U.S. Patent 4,943,303 which is hereby incorporated herein by reference for disclosure of such additives.

Additive compositions of the present invention are made by mixing components (A) and (B). In one embodiment, the mixing may take place in the fuel after each component of the additive composition is added separately to the fuel. In another embodiment, the components of the additive composition are first mixed, together with other additives if desired, to form the additive composition which is subsequently combined with the fuel. In yet another embodiment, at least some of the oil (B) is present in the reaction mixture, serving as a diluent during preparation of the dispersant (A).

The additive composition comprises from about 35 to about 55 parts by weight of the dispersant (A) and from about 30 to about 200 parts by weight of the oil (B). In a preferred embodiment, the additive composition comprises from about 20 35 to about 40 parts by weight of (A) and from about 60 to about 90 parts by weight of (B).

Additive compositions of this invention are used in the fuel in amounts sufficient to provide from about 35 to about 55 parts by weight of (A) a hydrocarbyl substituted succinimide dispersant containing from about 30 to about 200 carbon atoms in the hydrocarbyl group and from about 75 to about 40 parts by weight of (B) an oil having viscosity ranging from about 100 to about 400 centistokes at 40°C, each per million parts by weight of fuel oil.

The following examples illustrate fuel compositions, including a "good" baseline composition, comparative fuel compositions and fuel compositions of this invention. The base fuel used is Cat 1K Reference Fuel. The indicated products and added oil, if used are blended into the base fuel. The amounts of dispersant on a neat, diluent free basis and total oil or solvent are listed for each composition.

Amounts of Dispersant (A), Oil (B) and Solvent are in parts per million parts (ppm) of fuel.

| Fuel Example | Product of Ex (ppm) | Added Oil | Dispersant (A) | Oil (B) | Solvent |
|--------------|---------------------|-------------------|----------------|---------|---------|
| Baseline | 1 (100) | 0 | 60 | 40 | 0 |
| 1 | 1 (60) | 40 ¹ | 36 | 64 | 0 |
| Comp 1 | 1 (80) | 0 | 48 | 32 | 0 |
| Comp 2 | 2B (80) | 0 | 56 | 0 | 24 |
| Comp 3 | 1 (50) | 70 ⁽¹⁾ | 30 | 90 | 0 |
| Comp 4 | 3 (80) | 0 | 56 | 0 | 24 |
| Comp 5 | 4 (80) | 0 | 56 | 24 | 0 |

⁽¹⁾ 330N Mineral oil

5 The effectiveness of the additive compositions of this invention to improve diesel engine fuel injectors is determined using the Cummins (Cummins Corp., Columbus, IN, USA) L-10 injector depositing test. This test utilizes two Cummins L-10 engines mounted in a tandem configuration, front to rear, connected flywheel to front crankshaft pulley adapter by a driveshaft. The operating conditions are 10 cyclic, with one engine driving the other in measured intervals. The maximum power generated by the operating engine is the frictional horsepower of the non-running engine. The test operates for a total of 125 hours. Test results include fuel flow data and deposit ratings from each fuel injector. A deposits rating of 10 or lower is desired.

15 The test is described in U.S. Patent 6,042,626. Specific details of this test are available from Engineering Test Services, a division of Cummins Engine Co., Charleston, SC, USA.

| Fuel Example | L-10 Result |
|--------------|-------------|
| Baseline | 9 |
| 1 | 9.1 |
| Comp 1 | 11.9 |
| Comp 2 | 14.2 |
| Comp 3 | 13.8 |
| Comp 4 | 15 |
| Comp 5 | 11.4 |

It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic sites of other molecules. The products formed thereby, 5 including the products formed upon employing the composition of the present invention in its intended use, may not susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

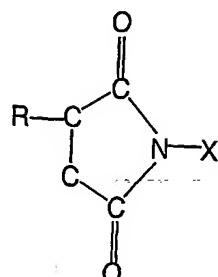
10 Each of the documents referred to above is incorporated herein by reference. Except in the examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about". Unless otherwise indicated, each chemical or 15 composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil which may be customarily present in the commercial material, 20 unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. As used herein, the expression "consisting essentially of" permits the inclusion of substances which do not materially affect the basic and novel characteristics of the composition under consideration.

25 While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications that fall within the scope of the appended claims.

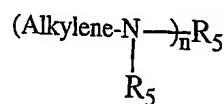
What is claimed is:

- 1 1. An additive composition for improving middle distillate fuel oils comprising
 - 2 (A) from about 35 to about 55 parts by weight of a hydrocarbyl substituted
 - 3 succinimide dispersant containing from about 30 to about 200 carbon atoms in the
 - 4 hydrocarbyl group and
- 5 (B) from about 75 to about 40 parts by weight of an oil having viscosity
- 6 ranging from about 100 to about 400 centistokes at 40°C.
- 1 2. The additive composition of claim 1 wherein the hydrocarbyl group is an
- 2 aliphatic hydrocarbyl group.
- 1 3. The additive composition of claim 2 wherein the hydrocarbyl group contains
- 2 from about 30 to about 100 carbon atoms and is derived from homopolymerized
- 3 and interpolymerized C₂₋₁₈ olefins.
- 1 4. The additive composition of claim 3 wherein the polymerized olefins are 1-
- 2 olefins.
- 1 5. The additive composition of claim 4 wherein the 1-olefins are selected from
- 2 the group consisting of ethylene, propylene, 1-butene, isobutylene, and mixtures
- 3 thereof.
- 1 6. The additive composition of claim 2 wherein the hydrocarbyl group is a
- 2 polyisobutenyl group having \overline{M}_n ranging from about 400 to about 2,500.

1 7. The additive composition of claim 1 wherein the succinimide has the general
 2 formula



3
 4 wherein R is a hydrocarbyl group containing from about 30 to about 200 carbon
 5 atoms, and wherein the group X is selected from the group consisting of H, aliphatic
 6 hydrocarbyl containing from 1 to about 30 carbon atoms and



7
 8 wherein n has an average value between about 1 and about 10, the "Alkylene" group
 9 has from 1 to about 10 carbon atoms, and each R_5 is independently hydrogen or an
 10 aliphatic or amino aliphatic group containing up to about 30 carbon atoms.

1 8. The additive composition of claim 7 wherein the "Alkylene" group is an
 2 ethylene or propylene group.

1 9. The additive composition of claim 1 wherein the oil (B) is a mineral oil
 2 having viscosity ranging from about 300 to about 350 centistokes at 40°C.

1 10. A fuel composition comprising a major amount of a middle distillate fuel oil
 2 and a sufficient amount of the additive composition of claim 1 to provide from about
 3 35 to about 55 parts by weight of (A) a hydrocarbyl substituted succinimide
 4 dispersant containing from about 30 to about 200 carbon atoms in the hydrocarbyl
 5 group and
 6 (B) from about 75 to about 40 parts by weight of an oil having viscosity ranging
 7 from about 100 to about 400 centistokes at 40°C parts by weight, each per million
 8 parts by weight of fuel oil.

1 11. The fuel composition of claim 10 comprising from about 75 to about 130
2 parts by weight of the additive composition of claim 1 per million parts by weight of
3 fuel oil.

1 12. The fuel composition of claim 10 wherein the middle distillate fuel oil is a
2 diesel oil.

1 13. A method for reducing fouling of fuel oil injectors comprising fueling a
2 device equipped with said injectors with the fuel composition of claim 10.

1 14. A method of operating a compression-ignition engine comprising providing
2 as the fuel the fuel oil composition of claim 10 thereby reducing fouling of fuel oil
3 injectors of said engine.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/22520

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/14 C10L10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|--|-----------------------|
| X | WO 93 06194 A (CHEVRON RES & TECH) 1 April 1993 (1993-04-01) page 7, line 14 -page 8, line 23 | 1-9 |
| X | US 5 752 989 A (HENLY TIMOTHY J ET AL) 19 May 1998 (1998-05-19) column 3, line 38 -column 4, line 50; claim 36 column 6, line 1 - line 19 column 10, line 14 -column 11, line 3 | 1-8, 10-14 |
| X | GB 2 259 522 A (ETHYL PETROLEUM ADDITIVES INC) 17 March 1993 (1993-03-17) page 6, line 9 -page 7, line 12 page 9, line 12 - line 22 | 1-6 -/- |

Further documents are listed in the continuation of box C

Patent family members are listed in annex.

° Special categories of cited documents:

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Date of the actual completion of the international search

20 December 2001

Date of mailing of the international search report

03/01/2002

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/22520

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ^a | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------------------|--|-----------------------|
| X | US 5 679 116 A (CUNNINGHAM LAWRENCE J ET AL) 21 October 1997 (1997-10-21) column 11, line 64 -column 12, line 32; example 1 --- | 1-6,9 |
| X | US 4 325 708 A (BAGNETTO JR LUCIEN J) 20 April 1982 (1982-04-20) column 1, line 42 - line 61; claim 3 --- | 1-6 |
| A | US 5 114 435 A (ABRAMO GUY P ET AL) 19 May 1992 (1992-05-19) the whole document --- | 1-8,10 |
| A | GB 1 486 144 A (CITIES SERVICE OIL CO) 21 September 1977 (1977-09-21) the whole document --- | 1-8 |
| A | EP 0 526 129 A (ETHYL PETROLEUM ADDITIVES INC) 3 February 1993 (1993-02-03) page 5, line 1 - line 16 --- | 1-6 |
| A | WO 90 10051 A (UNION OIL CO) 7 September 1990 (1990-09-07) claim 17 --- | 1 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 01/22520

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|------------------|---|--|
| WO 9306194 | A 01-04-1993 | AT 140475 T CA 2095545 A1 DE 69212297 D1 DE 69212297 T2 EP 0557516 A1 ES 2090694 T3 JP 6502888 T WO 9306194 A1 US 5393309 A | 15-08-1996 14-03-1993 22-08-1996 06-02-1997 01-09-1993 16-10-1996 31-03-1994 01-04-1993 28-02-1995 |
| US 5752989 | A 19-05-1998 | CA 2221087 A1 | 21-05-1998 |
| GB 2259522 | A 17-03-1993 | AU 657356 B2 AU 2352592 A CA 2077616 A1 JP 5194967 A | 09-03-1995 18-03-1993 17-03-1993 03-08-1993 |
| US 5679116 | A 21-10-1997 | AU 3833793 A CA 2095683 A1 DE 69319275 D1 DE 69319275 T2 EP 0569228 A1 JP 7268365 A US 5551957 A | 11-11-1993 07-11-1993 30-07-1998 12-11-1998 10-11-1993 17-10-1995 03-09-1996 |
| US 4325708 | A 20-04-1982 | NONE | |
| US 5114435 | A 19-05-1992 | AU 4732789 A EP 0376578 A1 JP 2276892 A NZ 231731 A | 05-07-1990 04-07-1990 13-11-1990 26-03-1991 |
| GB 1486144 | A 21-09-1977 | JP 909628 C JP 51114405 A JP 52038843 B | 08-05-1978 08-10-1976 01-10-1977 |
| EP 0526129 | A 03-02-1993 | AU 654569 B2 AU 2059792 A CA 2074208 A1 DE 69202642 D1 DE 69202642 T2 EP 0526129 A1 ES 2073248 T3 JP 5194966 A | 10-11-1994 04-02-1993 30-01-1993 29-06-1995 12-10-1995 03-02-1993 01-08-1995 03-08-1993 |
| WO 9010051 | A 07-09-1990 | WO 9010051 A1 | 07-09-1990 |